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Thermogravimetric analysis of the behavior of sub-bituminous coal and cellulosic ethanol residue during co-combustion

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HIGHLIGHTS

- The co-combustion kinetics of sub-bituminous coal and CER was studied.
- Blending with cellulosic ethanol residue could improve the combustion performance.
- Two isoconversional kinetic models are proposed to obtain kinetic parameters.
- The lowest average activation energy was obtained by blending 20% CER.

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ABSTRACT

The influence of the addition of cellulosic ethanol residue (CER) on the combustion of Indonesian sub-bituminous coal was analyzed by non isothermal thermo-gravimetric analysis (TGA). The effect of blends ratio (5%, 10%, 15% and 20%), interaction mechanism, and heating rate (5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min) on the combustion process was studied. The results show that the increase of the blending ratio allows to achieve the increase of the combustibility index from 7.49E−08 to 5.26E−07 at the blending ratio of 20%. Two types of non-isothermal kinetic analysis methods (Ozawa–Flynn–Wall and Vyazovkin) were also applied. Results indicate that the activation energy of the blends decreases with increasing the conversion rate. In particular, the blending ratio of 20% confirms to have the better combustion performance, with the average value of the activation energy equal to 41.10 kJ/mol obtained by Ozawa–Flynn–Wall model and 31.17 kJ/mol obtained by Vyazovkin model.

1. Introduction

Coal is the most important primary energy source in power generation, with 36% of globally generated power. Its significance varies by world region: in the countries with large resource endowments, such as China or South Africa, the share of hard coal power generation is more than 80%. In rather import-dependent regions, such as Europe or Japan, the share is lower, but with 15% and 25%, respectively, coal plays a significant role in power generation as well (IEA CIAB, 2014). However coal combustion is one of the main causes of global warming. In particular, coal combustion is globally responsible for 43% of CO_2 emissions from fossil-fuel combustion, with 28% emitted from coal-fired power plants (Olivier et al., 2013).

In order to reduce CO_2 emissions, co-combustion offers a relatively low-cost solution and it is also an effective way of taking advantage of the high thermal efficiency of large coal fired boilers. Biomass combustion is considered carbon neutral, because the CO_2 released during combustion is theoretically withdrawn from the atmosphere by photosynthesis during the plant's growth.

Among biomass fuels, the cellulosic ethanol residue (CER) could be an interesting option. It is the main co-product of the ethanol production process from lignocellulosic biomass, Biochemical conversion of lignocellulose to ethanol is generally performed through microbial fermentation of sugars, generated by thermochemical pretreatment of the biomass, followed by an enzymatic hydrolysis of cellulose.

Ethanol is the most commonly used biofuel in internal combustion engines and the most widespread renewable transportation fuel in the world (Leboreiro and Hilaly, 2011). Currently, most of industrial scale ethanol production is based on energy crops, such as corn maize and sugar cane. However, the need to use non-food crops will lead to increase the next generation ethanol share and therefore a great amount of CER will be available. Usually the residue, mainly composed of lignin, is burned for energy generation in

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Nomenclature

α	conversion rate	f_2	fraction of cellulosic ethanol residue
β	heating rate (°C/min)	HHV	higher heating value
A	pre-exponential coefficient (s^{-1})	i	ignition
b	burnout	m	mass
CER	cellulosic ethanol residue	n	order of reaction
db	dry basis	R	gas constant (J/mol K)
DTG	differential thermogravimetric balance signal	S	combustion index
E	activation energy (kJ/mol)	t	time (s)
f_1	fraction of coal	T	temperature (°C)

a combined heat and power (CHP) unit, with lower efficiency, respect to existing coal-fired burners (Guo et al., 2013).

However the knowledge of the kinetics of combustion is a key element in planning coal and biomass fuel blends, because thermo-chemical processes depend both on the operating conditions and on the physical and chemical properties of the fuels. In particular, differences in terms of volatile matter and fixed carbon content between coal and CER could affect the combustion profiles of the related blends.

Thermogravimetric analysis (TG) is one of the most widespread technique for an initial evaluation of the combustion behavior of solid fuels (Xie and Ma, 2013; Slopiecka et al., 2012). Although the obtained results are difficult to directly transfer to other devices at industrial scale, thermogravimetric analysis is very useful for the comparison between different samples and/or blends (Gil et al., 2010). It allows to quickly determine the main parameters (such as temperatures at which the combustion process starts and ends, fuel reactivity) required for the proper boiler design and for the calculation of excess air, residence time, and combustion efficiency.

Several studies dealing with the application of TG analysis to evaluate combustion behavior of coal and biomass alone and their blends in co-firing application were reported in the Literature (Taş and Yűrűm, 2012; Vamvuka and Sfakiotakis, 2011). However, to improve our knowledge, TG analysis has never been applied to evaluate changes in combustion kinetics of coal when blended with CER.

In the present paper, the parameters affecting CER and sub-bituminous coal co-combustion were analyzed using TG analysis. The interaction was also evaluated under different blend ratios. By performing TG analysis at different heating rates, a kinetic assessment of the co-combustion process using Vyazovkin and Ozawa–Flynn–Wall (OFW) iso-conversional methods was carried out, in order to evaluate the combustion reactivity of the blended fuels. Results can provide useful information for the design and optimization of thermo-chemical conversion systems of these blends.

2. Methods

2.1. Materials and blends preparation

The feedstocks used in this study were an Indonesian sub-bituminous coal and CER. Coal was provided by ENEL power plant of Bastardo (Italy). CER was obtained from a large-scale pilot plant where steam-exploded wheat straw is converted into ethanol, with simultaneous saccharification and fermentation (SSF) process (Buratti et al., 2014). In particular, wheat straw was firstly pretreated via steam explosion without acid impregnation, in order to increase enzyme accessibility to the cellulose and promoting the hemicellulose separation in a liquid fraction. The solid fraction was then subjected to SSF process, obtaining CER (composed of lignin, ash and unreacted carbohydrates) as waste product.

Both samples were oven-dried at 105 °C for 8 h and then they were milled in a rotor mill (Retsch ZM 200) and sieved to <500 μm. Blends were then prepared by physical mixing, with different weight percentages of CER (95C5CER: 5%, 90C10CER: 10%, 85C15CER: 15%, 80C20CER: 20%) which are typical of co-firing applications in European industry (Vamvuka and Sfakiotakis, 2011). In fact, at percentages higher than 20% wt, slagging, fouling and corrosion problems, arising from biomass combustion, should be carefully evaluated (Dai et al., 2008).

Each sample was subjected to proximate, ultimate analysis and calorimetry. Proximate analysis allowed to obtain moisture, volatile matter, ash, and fixed carbon content, according to ASTM D 5142, using a thermogravimetric analyzer (TGA-701, LECO Co., USA). Ultimate analysis was carried out for the determination of carbon, hydrogen, and nitrogen content, according to ASTM D 5373-02, using an elemental analyzer (TruSpec, LECO Co., USA). Higher heating values were measured by calorimetry, using a bomb calorimeter (AC-350, LECO Co., USA), according to the standard ASTM D 5865-04.

Since the content of hemicellulose, cellulose and lignin significantly affects biomass thermal behavior in the combustion process, the determination of these three main constituents was performed, according to NREL laboratory analytical procedures (Sluiter et al., 2008).

2.2. Thermogravimetric analysis

Combustion characteristics of sub-bituminous coal, CER and their blends were determined in a Leco TGA 701 thermal analysis system, with a sample of 0.2 g under air atmosphere, with a flow rate of 3.5 L/min from 25 °C to 1000 °C. Each sample, placed in ceramic crucibles, was tested at four heating rates: 5, 10, 15, and 20 °C/min. At these conditions the residues left in the crucible after combustion are formed by loose particles, showing that there is no sign of melting behavior, caused by mass and heat transfer limitations (Zhang et al., 2013). The weight loss (TG curve) and the differential weight loss (DTG curve) were recorded continuously, as a function of time and temperature.

Duplicate experiments for each test were performed in order to test the reproducibility of the results and the results revealed that the reproducibility of each run was good and the relative deviation was generally within ±1.0%. In order to check whether interaction occurs during co-combustion, the theoretical DTG curve of each blend was calculated, based on a weighted average of the components (Lee et al., 2010):

$$\mathrm{DTG} = f_1 * \mathrm{DTG}_{\mathrm{coal}} + f_2 * \mathrm{DTG}_{\mathrm{biomass}} \tag{1}$$

where $\mathrm{DTG}_{\mathrm{coal}}$ and $\mathrm{DTG}_{\mathrm{biomass}}$ are the mass loss rates of each material and f_1, f_2 are the mass fraction of coal and CER in the blend, respectively.

2.3. Measurement of combustion parameters

Combustion performance of materials was analyzed by the determination of relevant combustion parameters, such as ignition temperature (T_i), burnout temperature (T_b) and the combustion index (S).

The ignition temperature was defined as the temperature at which the weight loss rate is 1%/min after the initial weight loss caused by the moisture. The burnout temperature was defined as the temperature at which the burning rate reaches 1%/min at the end of DTG curve (Moon et al., 2013). The combustion index was calculated by the following equation (Vamvuka and Sfakiotakis, 2011):

$$S = \frac{\mathrm{DTG_{max}} * \mathrm{DTG_{mean}}}{T_i^2 * T_b} \tag{2}$$

where $\mathrm{DTG_{max}}$ is the maximum combustion rate and $\mathrm{DTG_{mean}}$ is the average conversion rate between ignition and burnout temperatures, calculated using Eq. (3) (Taş and Yűrűm, 2012):

$$(\mathrm{d}m/\mathrm{d}t)_{\mathrm{mean}} = \frac{\alpha_{T_b} - \alpha_{T_i}}{((T_b - T_i)/\beta)} \tag{3}$$

where α_{T_b} and α_{T_i} are the fractions of material degraded at the burnout and ignition temperatures, respectively, and β is the heating rate.

A high value of ignition temperature means that the fuel is thermally stable and so it is difficult to ignite. Burnout temperature is the temperature at which the combustion is almost complete; high values of burnout temperature indicate that the fuel has difficulty to burn, requiring longer residence time and higher temperature for complete conversion. The combustion index is a parameter that takes into account both ignition and burnout properties of the fuel. In particular, high values of S mean better combustion performance.

2.4. Kinetic analysis

The reaction rate of a heterogeneous Arrhenius type reaction can be described as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Ae^{-\frac{E}{RT}} f(\alpha) \tag{4}$$

where α is the conversion degree, t is the time, T is the temperature, A is the pre-exponential factor, R is the ideal gas constant (8.314 J/mol K), E is the activation energy and $f(\alpha)$ is the function describing the reaction model. In particular, $\alpha(T)$ indicates the rate of the fuel undergoing the combustion reaction up to the temperature T and it could be calculated from data obtained in the TG analysis, according to the Eq. (5):

$$\alpha = \frac{m_0 - m_T}{m_0 - m_f} \tag{5}$$

where m_0 is the initial mass of the sample, m_T the mass of the sample at the temperature T and m_f the final mass of the sample.

The function $f(\alpha)$ is expressed as Eq. (6):

$$f(\alpha) = (1 - \alpha)^n \tag{6}$$

where n is the reaction order in the non-isothermal experiment.

Eq. (4) can be converted into non-isothermal rate, describing reaction rate as a function of temperature at a constant heating rate β (=dT/dt):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \tag{7}$$

Integrating the differential non-isothermal rate law produces the integral form of the non-isothermal rate law:

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_{T_0}^{T} e^{-\frac{E}{RT}} \mathrm{d}T \tag{8}$$

where $g(\alpha)$ is the integral function of conversion and T_0 is the initial temperature of the combustion reaction.

Several methodologies have been proposed for the calculation of the kinetic parameters A, E, and n, from the TG analysis, based on the Eq. (8). In particular, the kinetics of combustion reactions can be determined by single-heating rate methods (model-fitting) or multi-heating rate methods (isoconversional). Model-fitting methods require the knowledge of the reaction mechanism before its application, that is hardly to define precisely. Instead, isoconversional methods do not require any prior assumptions about the model function to obtain the kinetics parameters, and only requires a set of experimental data obtained at least three heating rates.

Since it has been shown that in solid-state reactions these kinetic parameters vary with the reaction progress (α) and the activation energy varies with heating rate due to mass/energy transfer effects (Vyazovkin, 2000), these variations can be detected by isoconversional methods.

In particular, in this study the activation energy associated to the thermal decomposition process of coal, CER, and their blends was evaluated by two different isoconversional models: Ozawa–Flynn–Wall (OFW) (Ozawa, 1965; Flynn and Wall, 1966) and Vyazovkin (Vyazovkin and Wight, 1998) kinetic models.

The OFW model is based on the Doyle's approximation (Doyle, 1961). Taking the common logarithm of Eq. (8) and substituting Doyle's approach, the Eq. (9) is obtained:

$$\log\beta = \log\frac{AE}{g(\alpha)R} - 2.315 - 0.457\frac{E}{RT} \tag{9}$$

For a given conversion degree, by plotting $\log\beta$ versus $1/T$, the activation energy can be obtained from the slope of the resulting straight line, without specifically knowing reaction mechanism.

According to the Vyazovkin model, since $E/2RT \gg 1$, the temperature integral can be approximated by:

$$\int_{T_0}^{T} e^{-\frac{E}{RT}} \mathrm{d}T \approx \frac{R}{E} T^2 e^{-\frac{R}{RT}} \tag{10}$$

Substituting the temperature integral, rearranging and logarithming, the Vyazovkin equation is obtained:

$$\ln\frac{\beta}{T^2} = \ln\left[\frac{RA}{Eg(\alpha)}\right] - \frac{E}{RT} \tag{11}$$

Table 1
Properties of CER and Indonesian sub-bituminous coal.

Material	CER	Indonesian sub-bituminous coal
Proximate analysis		
Ash (wt%)	8.1	3.0
Volatile matter (wt%)	78.4	50.2
Fixed carbon (wt%)	13.5	46.8
Ultimate analysis		
C (wt%)	49.4	71.5
H (wt%)	5.2	4.9
N (wt%)	1.2	0.9
S (wt%)	0.0	0.1
O by difference (wt%)	44.2	22.5
Calorific value		
HHV (MJ/kg)	20.9	28.7
Compositional analysis		
Cellulose (wt%)	26.0	–
Hemicellulose (wt%)	2.2	–
Lignin (wt%)	64.1	–
Other (wt%)	7.7	–

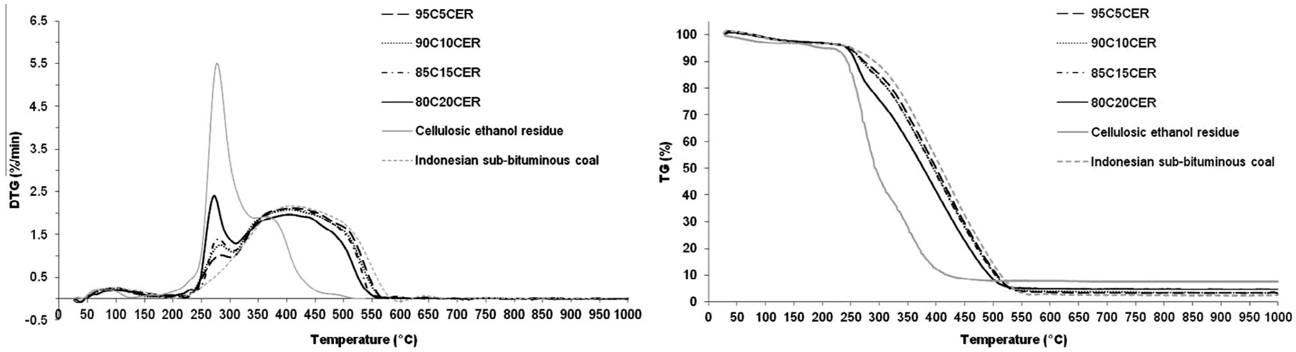

Fig. 1. Comparison of the TG–DTG curves of CER, Indonesian sub-bituminous coal and their blends at the heating rate of 5 °C/min: DTG curve (left); TG curve (right).

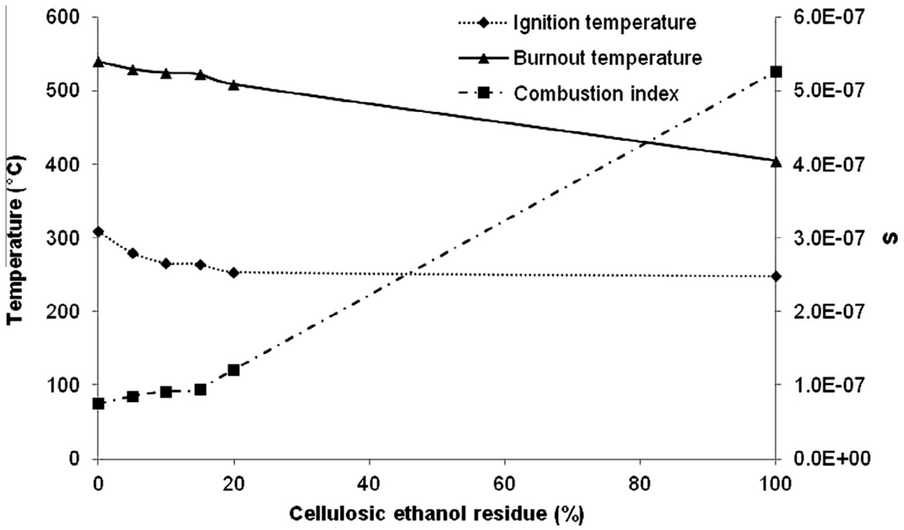

Fig. 2. Combustion characteristics of CER-Indonesian sub-bituminous coal blends.

For each conversion degree, $\ln(\beta/T^2)$ is plotted against $1/T$, that results in a straight line with slope $(-E/R)$, thus providing the activation energy as a function of conversion.

In order to calculate reaction order, Avrami theory (Ruitenberg et al., 2001) was applied, as follows:

$$\alpha(T) = 1 - \exp\frac{-k(T)}{\beta^n} \qquad (12)$$

Taking double logarithm and transposing, Eq. (4) is changed into the following:

$$\ln[-\ln(1-\alpha(T))] = \ln(A) - \frac{E}{RT} - n\ln(\beta) \qquad (13)$$

For a given temperature, by plotting $\ln[-\ln(1-\alpha(T))]$ versus $\ln\beta$ at different heating rates, the reaction order can be determined from the slope of the straight line.

3. Results and discussion

3.1. Characterization of the materials

Table 1 shows the chemical and physical characterization of coal and CER. From the proximate analysis it was found that CER has higher volatile matter and less fixed carbon content than Indonesian sub-bituminous coal. Therefore biomass sample on one side is characterized by higher reactivity and on the other side it has less amount of residue after the decomposition of the solid residue. The ash content of the CER is higher than the one of coal, affecting burning rate and causing fouling or aggregation.

The heating values of CER is lower than the one of coal, due to the lower content of carbon and the higher content of oxygen and hydrogen, as results from ultimate analysis (Munir et al., 2009). This is confirmed by calorimetry. However, the higher oxygen concentration implies higher thermal reactivity of the CER compared to coal (Haykiri-Acma and Yaman, 2008).

Higher nitrogen content in the CER implies more NO_x emissions during the combustion process, while lower sulphur concentration causes fewer emissions or corrosion during utilization.

In Table 1 the compositional analysis of the CER is also reported. Contents of cellulose, hemicellulose and lignin are significant parameters in the combustion process, because high percentages respectively can increase the devolatilization rate, reduce the ignition temperature, and promote the combustion of char correspondingly (Kai et al., 2011). Data show that CER is mainly composed by lignin and unreacted cellulose, while the hemicellulose fraction is mostly separated during the steam explosion pre-treatment process of wheat straw.

3.2. Combustion process of the pure samples

The TG and DTG profiles, obtained at a heating rate of 5 °C/min, of CER and Indonesian sub-bituminous coal individual combustion were shown in Fig. 1. There are substantial differences in the thermal behavior of the samples.

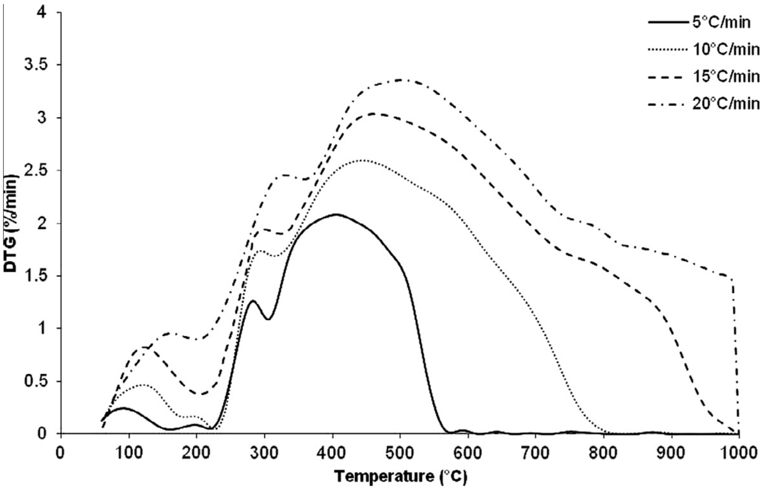

Fig. 3. DTG profiles for the blending ratio of 10% at different heating rates.

Table 2
Combustion parameters for the blending ratio of 10% at different heating rates.

Heating rate (°C/min)	T_i (°C)	T_f (°C)	S
5	266	525	9.20E−08
10	261	708	1.04E−07
15	254	896	1.07E−07
20	229	993	1.49E−07

In particular, the thermal degradation of CER is characterized by three main zones. The first zone extends up to the temperature of about 125 °C, related to the evaporation of the inherent moisture and the release of the volatile compounds. In the range 125–340 °C a significant peak, corresponding to the decomposition of cellulose and hemicellulose, was detected. This stage represents the release of volatiles and their ignition leading to char formation. It is well known that the decomposition of the main components of biomass (hemicellulose, cellulose, and lignin) occurs in the range of 225–325 °C, 305–375 °C, and 250–500 °C, respectively (Prins et al., 2006). Therefore the second zone is dominated by the thermal degradation of hemicellulose and cellulose. Since the hemicellulose content of the CER is much lower compared to other lignocellulosic biomass, the devolatilization stage shifts to lower temperatures and the DTG curve does not show the typical shoulder peak (Kai et al., 2011). The third zone is the widest stage (340–515 °C) where the lignin degradation occurs. Lignin is the most thermal stable component of biomass and it is the main responsible for biomass char formation (Sanchez-Silva et al., 2012). In particular the small peak of the weight loss rate confirms the low reactivity of lignin, since the reactivity is inversely proportional to the temperature corresponding to peak (DTG peak) and directly proportional to the peak height.

Indonesian sub-bituminous coal shows an initial mass loss between the temperatures 25–205 °C, due to moisture removal. Then the thermal degradation of the coal shows only one major peak over a wide temperature range (205–585 °C), which represents the release of carbon containing volatile matter from coal (Bhagavatula et al., 2014) and the temperature corresponding to the maximum DTG is approximately 410 °C. Since Indonesian sub-bituminous coal has a high volatile content, the weight loss is determined by combustion of solid carbon and volatilization in the whole process; therefore DTG has a single peak. In particular, the maximum weight loss rate is much lower than the one of CER, since Indonesian sub-bituminous coal contains a lower content of volatile matter.

From the TG curves, it can be seen that when CER burns almost completely (90%–422 °C), the weight loss of Indonesian sub-bituminous coal is around 44.5%. Furthermore the residual mass of Indonesian sub-bituminous coal and CER at the end of the combustion process were respectively 2.64% and 7.55%, consistent with their ash content. The blends of highly reactive fuels, such as CER, with coal could help to initiate the combustion process of coal. Therefore, investigation of these effects is very important for co-firing applications.

3.3. Co-combustion of Indonesian sub-bituminous coal-CER blends

The TG and DTG profiles of the blends at the heating rate of 5 °C/min are also shown in Fig. 1. Comparing the DTG curves of the blends with the one of coal, it can be seen that the first are characterized by two oxidation zones: the first one in the 220–310 °C due to the hemicellulose and cellulose degradation, and the second wider one stage, up to about 570 °C, mainly due to the release of volatile matter in the coal, which burns slowly over the whole temperature range, together with the char. All the curves of the blends lie between the ones of the pure samples and, as the weight percentage of the CER increases, the combustion profiles of the blends become more similar to the one of the biomass sample.

Fig. 2 shows the combustion parameters of the single fuels and their blends, calculated from the TG and DTG curves. It can be seen that with the increase in CER proportion, the ignition and burnout temperatures of blends decrease, due to the higher reactivity of CER. In particular, the decrease in ignition temperature is caused by the improvement in the devolatilization characteristics of blends with the addition of CER. The reduction in the burnout temperature is quite proportional to the percentage of CER in the blends, while this is not valid for the ignition temperature. In fact volatile release temperature depends on some other factors, such as availability of oxygen and particle heating rate (Marisamy et al., 2010). Fig. 2 shows also the maximum weight loss rate (DTG_{max}); it can be observed that blending CER with coal does not lead to significant changes up to the ratio of 15%. Above this value the maximum weight loss rate peak of the blends shifts from the hemicellulose peak to cellulose peak.

As the maximum weight loss temperature, the combustion index of the blended fuel did not show a linear relationship with blend ratio. In particular, up to the ratio of 15% the combustibility of the blends is slightly improved by the CER, while the difference is stronger for the blending ratio of 20%.

Table 3
Activation energy obtained from OFW and Vyazovkin methods for the combustion of the fuels and the blends.

Sample	α (%)	OFW			Vyazovkin		
		Slope	E_a (kJ/mol)	R^2	Slope	E_a (kJ/mol)	R^2
Coal	0.2	−9.77	77.25	0.8801	−8.51	70.78	0.8707
	0.3	−7.69	60.79	0.9466	−6.35	52.76	0.9222
	0.4	−6.05	47.84	0.9771	−4.63	38.47	0.9589
	0.5	−5.05	39.95	0.9839	−3.54	29.46	0.9632
	0.6	−4.29	33.88	0.9851	−2.69	22.34	0.9537
	0.7	−3.66	28.92	0.9824	−1.95	16.24	0.9198
	0.8	−3.26	25.77	0.9836	−1.44	11.98	0.8830
	Average		44.91			34.57	
95C5CER	0.2	−10.71	84.65	0.9842	−9.48	78.80	0.9802
	0.3	−7.33	57.95	0.9990	−6.01	49.96	0.9988
	0.4	−5.73	45.30	0.9998	−4.33	35.96	0.9994
	0.5	−4.76	37.65	0.9995	−3.27	27.22	0.9978
	0.6	−4.07	32.17	0.9988	−2.49	20.71	0.9933
	0.7	−3.48	27.53	0.9960	−1.79	14.92	0.9718
	0.8	−3.14	24.81	0.9959	−1.33	11.07	0.9500
	Average		44.30			34.09	
90C10CER	0.2	−11.72	92.66	0.9805	−10.51	87.36	0.9760
	0.3	−7.52	59.46	0.9971	−6.22	51.67	0.9958
	0.4	−5.81	45.93	0.9993	−4.42	36.74	0.9988
	0.5	−4.82	38.11	0.9999	−3.35	27.82	0.9940
	0.6	−4.12	32.58	0.9997	−2.56	21.25	0.9973
	0.7	−3.55	28.07	0.9983	−1.88	15.61	0.9852
	0.8	−3.19	25.18	0.9977	−1.39	11.57	0.9680
	Average		46.00			36.01	
85C15CER	0.2	−13.77	108.82	0.9486	−12.56	104.42	0.9387
	0.3	−7.88	62.30	0.9743	−6.58	54.69	0.9627
	0.4	−5.88	46.50	0.9853	−4.49	37.36	0.9732
	0.5	−4.83	38.14	0.9901	−3.35	27.86	0.9763
	0.6	−4.09	32.31	0.9908	−2.52	20.96	0.9687
	0.7	−3.48	27.52	0.9872	−1.81	15.01	0.9347
	0.8	−3.10	24.51	0.9848	−1.30	10.82	0.8798
	Average		48.59			38.73	
80C20CER	0.2	−9.51	75.13	0.8771	−8.33	69.23	0.8938
	0.3	−6.57	51.93	0.9464	−5.31	44.12	0.9217
	0.4	−5.30	41.85	0.9839	−3.94	32.80	0.9737
	0.5	−4.44	35.06	0.9589	−3.00	24.97	0.9196
	0.6	−3.97	31.40	0.9974	−2.45	20.33	0.9948
	0.7	−3.48	27.52	0.9982	−1.85	15.34	0.9882
	0.8	−3.14	24.78	0.9966	−1.37	11.38	0.9578
	Average		41.10			31.17	
CER	0.2	−20.64	163.13	0.9999	−19.58	162.76	0.9999
	0.3	−13.81	109.12	0.9999	−12.70	105.61	0.9999
	0.4	−10.47	82.76	0.9999	−9.33	77.56	0.9999
	0.5	−10.17	80.36	0.9731	−8.97	74.58	0.9660
	0.6	−5.36	42.33	0.9799	−4.07	33.81	0.9628
	0.7	−3.94	31.12	0.9966	−2.56	21.29	0.9888
	0.8	−3.45	27.29	0.9981	−1.97	16.42	0.9881
	Average		76.59			70.29	

Therefore, a high reactivity fuel, such as CER, could improve the combustion of Indonesian sub-bituminous coal; however, combustion behaviour of the blend cannot be easily predicted from fuels ratio.

3.4. The influence of heating rate on the co-combustion

The DTG curves at different heating rates (5, 10, 15, and 40 °C/min) for the blending ratio of 10% are shown in Fig. 3. Table 2 shows the combustion properties under different heating rates. As the heating rate increased, the DTG curves were translated to higher temperatures, according to the results reported in the Literature (López et al., 2013). In particular both stages of the combustion process are developed in a wider temperature range, when increasing the heating rate.

Therefore, heating rate has an important role in the devolatilization and combustion stages of the blends, because it can accelerate devolatilization rate, but the complete oxidation of char requires more time.

In particular, ignition temperature tends to slightly decrease with increasing the heating rate, while the burnout temperature shifts from 525 °C at 5 °C/min to 993 °C at 20 °C/min.

In fact at high heating rate, the heat transfer inside the particles is less effective while at lower heating rate it improves.

The fact that the maximum mass loss rate and combustion index shift toward high values, prove that combustion intensity can be improved increasing heating rate. Higher heating rate implies a shorter time to achieve a certain ambient temperature, which leads to a relative larger temperature difference between ambient (or surface) and core of a particle, due to non isothermal behavior of the samples. Therefore heating rate definitely enhances heat transfer from surface to the core of the particle.

3.5. Analysis of kinetic parameters

The effect of blending ratio on the combustion process was evaluated through OFW and Vyazovkin methods. According to

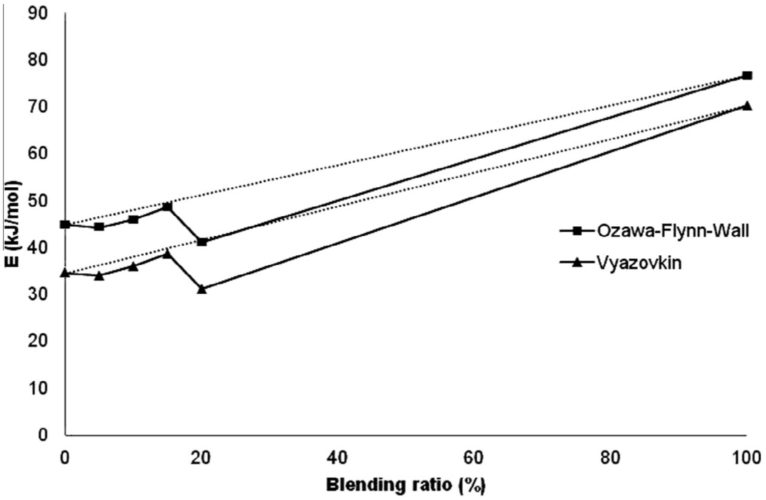

Fig. 4. Average activation energy versus blending ratio of CER, determined by OFW and Vyazovkin methods.

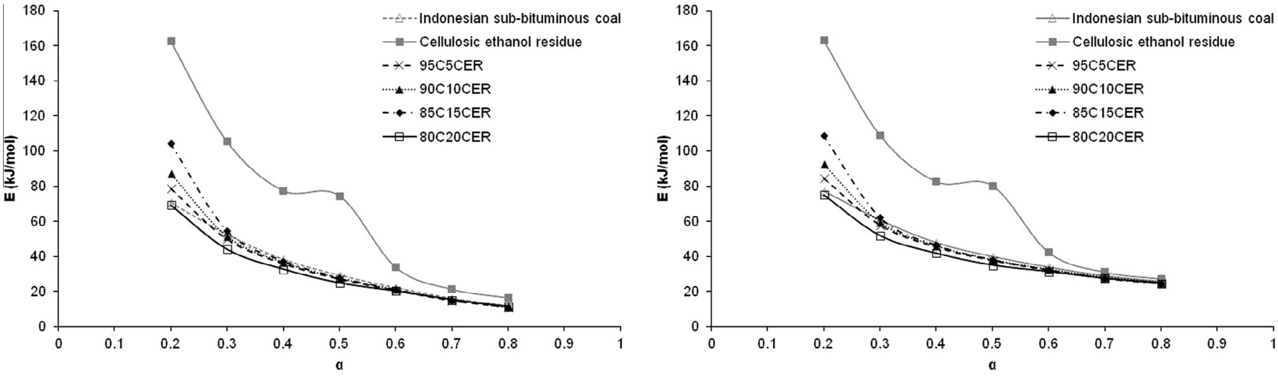

Fig. 5. Activation energy versus the conversion rate of fuels during combustion (OFW method on the left, Vyazovkin on the right).

Table 4
Reaction order versus temperature.

Temperature (°C)	Indonesian sub-bituminous coal	95C5CER	90C10CER	85C15CER	80C20CER	CER
380	0.525	0.767	0.568	0.553	0.635	0.599
430	0.799	0.785	0.753	0.743	0.775	0.688
Average *n*	0.662	0.776	0.661	0.648	0.705	0.644

Eqs. (9) and (11), activation energy values were calculated adopting heating rates of 5, 10, 15 and 20 °C/min. Only the α values in the range 0.2–0.8 were considered, because data outside this range had a poor correlation coefficient. Table 3 shows the slopes of linear fittings for each degree of conversion and corresponding activation energy values. The average value of E was obtained as the arithmetic mean of several values, corresponding to various degrees of conversion. As it is shown in Table 3, the activation energies obtained from both methods had good correlation coefficients (R^2) in the range of 0.8707–0.9999 and most of them were larger than 0.9600, showing acceptable accuracy of results.

The activation energy values reported in Table 3 are not related to any single reaction step, but they are aggregated values, reflecting the contributions of parallel reaction steps on the overall reaction rate.

It is known that, for complex processes such as solid fuels combustion, each contribution can change with temperature and degree of conversion, often overlapping each other. This factor reduces the utility of such global kinetic parameters for the evaluation of the decomposition mechanisms because no particular reactions can be defined (Aboyade et al., 2011). However, this analysis allows to obtain some general tendencies, through the comparison of fuels reactivity. As it may be seen, activation energy values obtained through the application of Vyazovkin model were all lower than the ones obtained through OFW model, but with the same trend. In general, for solid fuels, different kinetic methods can give different results in terms of activation energy, because of heterogeneity of the samples and experimental conditions (Kök and Özgür, 2013). The activation energy value during combustion process of Indonesian sub-bituminous coal is 44.91 and 34.57 kJ/mol, estimated through OFW and Vyazovkin methods, respectively. These values are high, when compared to data in the Literature (Otero et al., 2008), however the lower activation energy found for the Indonesian sub-bituminous coal could be due to its high volatile matter and reactivity (Binner et al., 2011).

CER combustion activation energy is lower if compared to data previously reported for other biomasses (López et al., 2013; Wang et al., 2012); this is mainly due to its high content of lignin, which

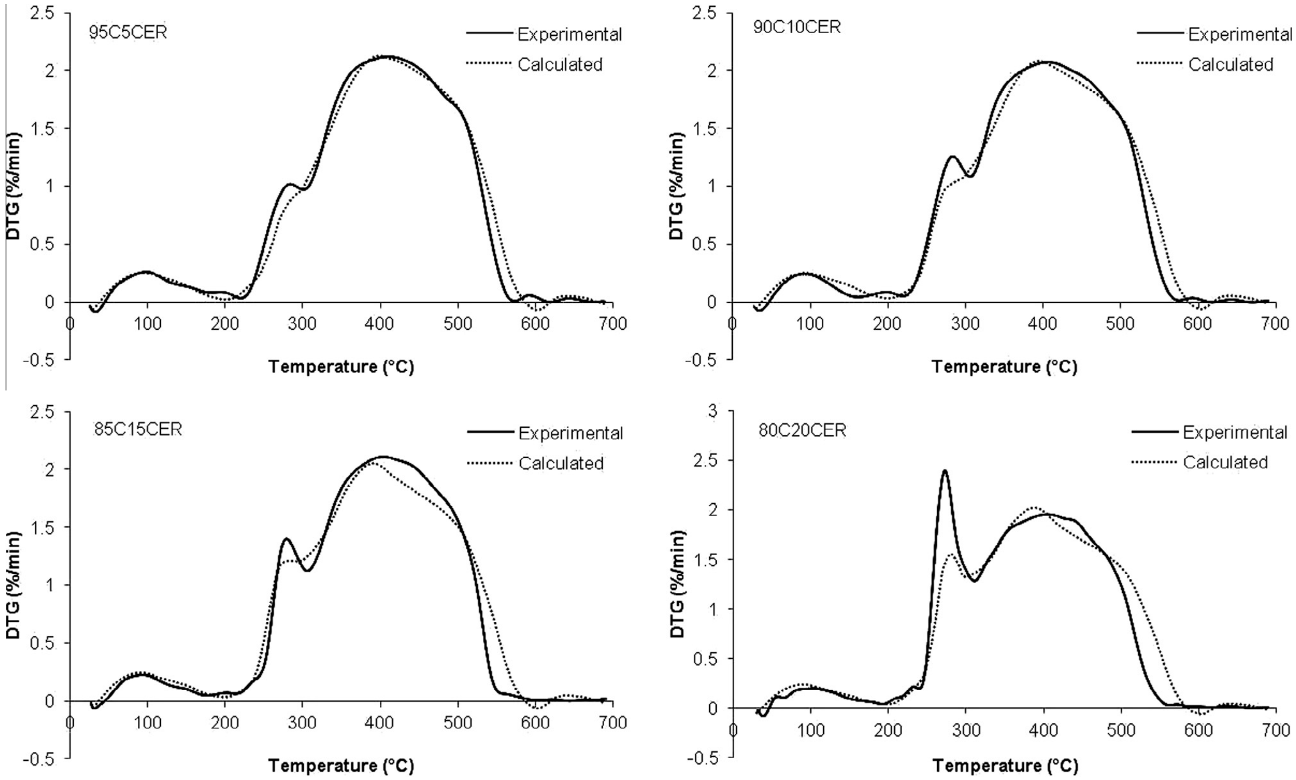

Fig. 6. The comparison of experimental and calculated DTG curves for the blends at the heating rate of 5 °C/min.

has an activation energy value (18–65 kJ/mol) lower than cellulose (195–286 kJ/mol) and hemicellulose (80–116 kJ/mol) (Gronli et al., 2002).

Activation energy (*E*) average value, as a function of the blending ratio of CER is shown in Fig. 4: it does not monotonically increase with the increase of blending ratio. The same trend is confirmed by the two methods. The dotted lines in Fig. 4 were the predicted value of the activation energy, based on the weighted average of the coal and CER.

A significant decreasing peak was observed between the predicted and experimental mean activation energy of the blend 80C20CER, due to the interaction between coal and CER. The values obtained for this particular blend are: 41.10 kJ/mol by OFW and 31.17 kJ/mol by Vyazovkin. Being this value less than the one of coal, this blending ratio could be potentially an optimal option for co-combustion. This result was interesting and only partly in agreement with the current Literature. Guangwei et al. (2013) found that the activation energy of the biomass char and anthracite coal blend first decreases and then increases with increasing content of biomass char and the lowest value is obtained for a content of biomass char equal to 60%. Taş and Yűrűm (2012) and Kocabaş Ataklı et al. (2015) reported a monotonic increasing trend of the activation energy with the increase of the biomass percentage in the blend.

It is also interesting to evaluate activation energy versus conversion rate (Fig. 5). Within the $\alpha = 0.2–0.8$ range, the values of activation energy for CER were consistently higher than the ones for coal. The shape of the curves obtained from the two methods is very similar. The blends show a trend similar to the one of coal, which mostly becomes the same for $\alpha > 0.6$.

The decreasing trend of activation energy at higher conversion rates agrees with the results reported in previous studies on biomass materials (Aboyade et al., 2011) and coals (Taş and Yűrűm, 2012), but contradicts a few others (Xie and Ma, 2013; Gil et al., 2010). This again highlights the unreliability of the mechanistic interpretation of the kinetic trends obtained from complex materials. Furthermore, the dependence of the activation energy on the degree of conversion confirms the multistage characteristic of the combustion process of fuels.

Reaction order is also an important kinetic parameter to describe combustion mechanism. It was calculated, according to Avrami theory, as explained in the previous section, plotting $\ln[-\ln(1-\alpha(T))]$ versus $\ln\beta$. Reaction order values as a function of temperature for Indonesian sub-bituminous coal, CER and their blends are reported in Table 4. Reaction orders were evaluated at two different values of temperature (380 °C and 430 °C), both in the range between ignition and burnout temperatures of the fuels. The values ranged from 0.5 to around 0.8 and are dependent on the extent of the reaction and on the type of material, which indicates the complexity of the degradation process of all these materials and highlights the multiple step process. While coal and CER have comparable reaction order values in the temperature range of combustion, 95C5CER has a higher one.

Finally, it must be taken into account that kinetic parameters determined in this study were obtained from reaction rates characterized only by temperature, not taking into account mass transfer and structural transient variations. Anyway, although specific combustion operation conditions should be specifically studied in experimental reactors, the obtained information must be first taken into account when planning co-firing of these materials.

3.6. Interactions between the components of the blends

In order to confirm interactions between components of the blends found in the activation energy analysis, theoretical DTG curves of the blends were calculated according to the Eq. (1). Calculated and experimental curves for the blends at the heating rate of 5 °C/min are shown in Fig. 6.

The shape of the experimental curves resembles combustion curve of the component in a larger percentage. For all blends, the main deviations are represented by the greater peak height in the combustion zone, related to the hemicellulose and cellulose degradation and the shorter duration of the coal combustion stage. Therefore the blends have increased reactivities compared to expected values. These deviations tend to become more noticeable as the blending ratio increases.

Thus, all differences indicate that the combustion behavior of the blend could not be predicted by a simple linear correlation of the pure fuel characteristics. It can be deduced that mutual interaction exists between two components during the combustion.

4. Conclusions

CER was subjected to two combustion steps: between 125 °C and 340 °C, mainly due to the volatilization of hemicellulose and cellulose, and between 340 °C and 515 °C, above all due to the lignin decomposition. Instead, sub-bituminous coal was characterized only by one combustion step, (205–585 °C). OFW and Vyazovkin methods showed that the minimum value of the activation energy was achieved at CER equal to 20%, with a specific value of 41.10 kJ/mol using OFW method and 31.17 kJ/mol using Vyazovkin method. The study results can provide the reference for large-scale co-combustion and utilization of CER and coal.

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